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Optoelectronic properties and photo-physics of large grain hybrid perovskites

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1. Introduction

Organic-Inorganic or (Hybrid) perovskites are a special class of perovskites with a general chemical formula of AMX_3 formed by using low-temperature synthesis approaches. They exhibit exceptional fundamental properties that have been translated into proof-of-principle demonstrations of photovoltaics (*1*), light emitting diodes(*2*), photodetectors(*3*), thermoelectric devices, lasers(*4*), photo-catalysts(*5*) and gamma ray detectors(*6, 7*) among which energy harvesting in photovoltaics has been the most studied(*1, 8-15*). While tremendous progress is being made, a fundamental bottleneck in that has existed in field is the high degree of variability in crystalline quality, grain-size, and microstructure of hybrid perovskites reported by the community. This has resulted in multiple interpretations of experimental data and thus key fundamental mechanisms remain largely unresolved. An ideal solution to this issue of non reliable properties is the ability to reproducibly grow hybrid perovskite thin-films with high degree of crystallinity, which allow access to the intrinsic physical properties, which are otherwise masked by non-reliable processing dependent microstructure. Here we present our recently developed fast thin-film crystal growth technique termed as hot-casting, which allows us to grow high crystalline quality, uniform, pinhole free films of hybrid perovskites with hundreds of microns to mm-scale grain-size. Investigation of photo-physical properties reveals that the resulting large grains behave as classical III-V direct band-gap semiconductors. However, as the grain-size decreases, the properties can no longer be described using models described for direct gap semiconductors. When incorporated into a simple "inverted" photovoltaic bilayer architecture with ITO/PEDOT:PSS/Perovskite/PCBM/Al, with no minimal optimization a hysteresis free device with a current-voltage curve of 15.37%. Electrical characterization using capacitance-voltage measurements and light-intensity dependence of the open circuit voltage suggest that perovskite films are intrinsic and the photogenerated charge carrier recombine through a bimolecular process, only observed in high quality semiconducting materials.

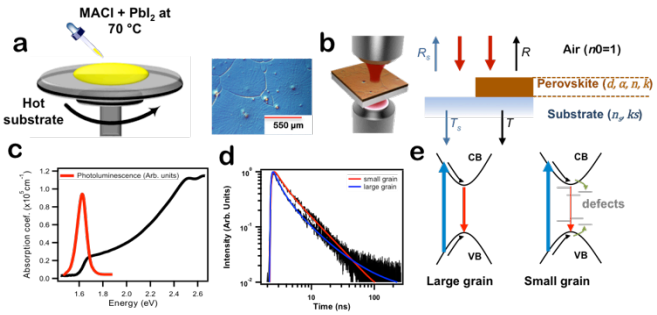

Fig. 1. Describes the hot-casting process and photo-physical measurements on hybrid perovskites. a) Illustrates the hot-casting process (left) and the optical micrograph (right) showing a typical thin-film with large grain-size. b) Shows the procedure for measuring absolute absorption using transient reflectivity where the stage is modulated such that the incident light samples the thin-film and the substrate. The change in transmission (and reflection) through the substrate and the perovskite thin-film is measured using a lock-in amplifier and results in a very accurate measurement of the absorption coefficient. c) Absolute absorbance (black) and photoluminescence (PL) spectra (red) of large grain perovskites reproduced from ref (*16*) d) time resolved PL of large (blue) and small (red) grains reproduced from ref (*16*).

Fig. 1a illustrates the hot-casting process (left) described elsewhere(*15*) and the corresponding optical image showing the perovskite thin-film with large grain size. Briefly, ITO/PEDOT: PSS substrates were heated inside an Argon glove box on a hot substrate maintained at a temperatures between 130 °C – 190 °C. The substrates are immediately (within 5 seconds) transferred onto a spin coater and precursors solution containing 1:1 molar ratio of MACl and PbI_2 were drop casted on to the substrate and spin coating was initiated (within 3 seconds). As the spin coating commences, the substrate temperature and the solvent temperature begin to quench. However, during this process, the presence of the solvent for a prolonged period allows for the perovskite molecules to diffuse and form large crystals. This is in sharp contrast to conventional post-annealing procedures where the post-annealing of the spin-coated precursor film (where the solvent is already dried) causes the immediate loss of the solvent, thus recuing the possibility for the molecules to diffuse and as a result leads to thin-films with grain-size typically in the sub-micron range. We

measured the absolute absorption of the resulting perovskite thin-film with large grains using the transient reflectivity technique (*16*) (Fig. 1b). The resulting absorbance as a function of excitation energy and the photoluminescence (PL) spectra is illustrated in Fig. 1c. The photoluminescence spectra and the absorbance spectra are nearly overlapped at the band-edge with a stokes shift of merely 5 meV. The small Stoke shift is a classic signature of a high quality semiconducting materials and validates that hot-casting results in perovskite thin-films reminiscence of classical III-V direct band-gap semiconductors. The time resolved PL decay for both large and small grain perovskites measured at an excitation density equivalent to the solar flux at AM 1.5G at 690 nm excitation wavelength is illustrated in Fig. 1d. For the large grains, the PL decay can be described using a simple second order rate equation with just one fitting constant, which is the bimolecular coefficient represented by A in the equation below.

$$(\frac{dN}{dt}) = G - AN^2 \qquad \textbf{(1)}$$

Here G is the generation rate of the photo-generated charge carriers at the band-edge. This suggests the all the light generated electron-hole pairs recombine to emit light as should be expected in a defect free direct band-gap semiconductor. Similar measurement performed on a perovskite thin-film with small grains cannot be described using the second order equation and requires an additional term (trap assisted recombination) to effectively fit the decay curve. Fig. 1e (left) describes schematically the recombination of electron-hole pairs across the band-gap in large grain-size perovskite thin-films and trap-assisted recombination in small grain-size perovskites where the photogenerated carriers recombine via defects (arising from grain boundaries or ionic vacancies due to inefficient conversion). These results supports the view that the solution processed hot-cast perovskite thin-films behave as classical direct band-gap materials. Here the PL quantum yield should be unity, however, because of strong reabsorption of the emitted photons, it is difficult to quantitatively estimate the quantum yield. We emphasize that it is important to perform these measurements at excitation densities relevant for solar cells (few SUNs) to evaluate the dynamic charge recombination processes in perovskite thin-films that can directly impact photovoltaic performance.

Fig. 2 describes the photovoltaic performance and electrical characterization of the hot-cast thin-films measured using in an inverted architecture (Fig. 2a). We measure an efficiency of 15.37% without any optimization of the device. Additionally do not observe any appreciable hysteresis in the current-voltage curves (Fig. 2b) and also in the capacitance-voltage measurements performed at two different frequencies (Fig. 2c). Capacitance measurements in the reverse bias indicate that the hot-cast perovskite film is intrinsic and can be described as a P-I-N junction. Moreover, we measure a built-in voltage of nearly 1.0 V, which is equal to the measured open circuit voltage (V_{OC}), suggesting the field across the P-I-N junction is strong enough to extract the photogenerated carriers. Finally, we measure the V_{OC} as a function of light intensity described by equation (2) for

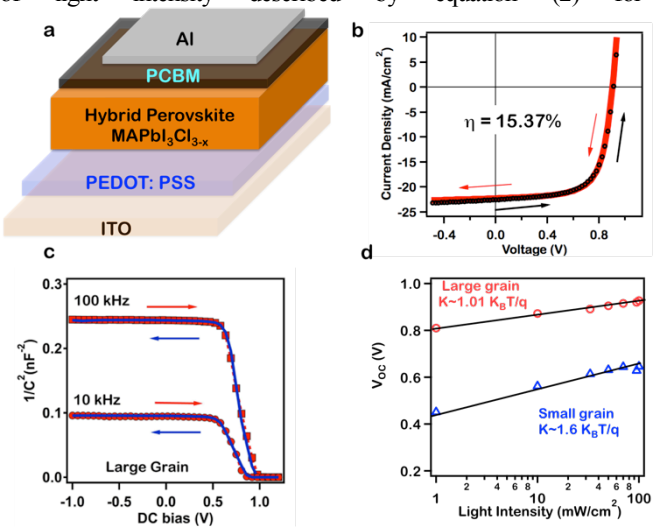

Fig. 2: Describes solar cell performance and characterization of hot-cast hybrid perovskite thin-films. a) Device architecture and b) J-V curves showing no hysteresis measured with AM 1.5G solar flux. c) Capacitance-voltage curves for large grains measured at two frequencies show that the perovskite film is intrinsic and d) V_{OC} as a function of light intensity validating that in large grain-size films, bimolecular recombination dominates and with decrease in grain-size, trap-assisted process appears.

large and small grain device (Fig. 2d). An n~1 for the large grains (red) indicates bimolecular recombination, consistent with the time-resolved PL measurements in fig. 1d and when n>1, trap assisted recombination dominates as observed in small grains (blue). The black lines represent the fit using equation (2).

$$V_{OC} \sim n(\frac{k_B T}{q})\ln(Intensity) \qquad \textbf{(2)}$$

In summary, we demonstrate that the hot-casting technique leads to perovskite thin-films with large grain-size that behaves like classical III-V semiconductors. More importantly, it allows access to the intrinsic optoelectronic properties in hybrid perovskite materials, which is often masked by detrimental effects like hysteresis and non-reproducible behavior emerging from processing dependent microstructural properties.

Acknowledgments

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